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SUPERCRITICAL FLUID EXTRACTION OF TRACE
ORGANICS FROM SOLID MATRICES

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Trace residue analysis of organic compounds in environmental solids is comprised of two steps; sample preparation and instrumental analysis. An autosampler can provide dedicated automation for instrumental analysis. However, the sample preparation, which involves sample extraction and purification is often the most time consuming and labor intensive operation in the analytical procedure. The extraction normally requires expensive organic solvents, is associated with human exposure to toxic chemicals, and is often not selective, a fact which necessitates the cleanup step. Supercritical fluids have shown promise of overcoming some of these difficulties in sample preparation.

A supercritical fluid is a fluid at a temperature and pressure above its critical values. Under these conditions, some fluids have properties which render them excellent solvents, even for solutes which are not soluble in them under ambient conditions. The advantages of using supercritical fluids for extraction stem mainly from the variation of density of a fluid with pressure near its critical point. Since the ability of a solvent to dissolve a solute increases with the density of the solvent, supercritical fluids offer the advantage over liquid solvents that solubilities can be varied by varying the pressure. The transport properties of a supercritical fluid are intermediate between those of the corresponding gas and liquid. Viscosities are considerably lower than those of the corresponding liquids, and diffusion coefficients are considerably higher. The kinetics of extraction of solutes from solid matrices are thus faster in supercritical fluids than in liquids. The variation of solubility with pressure in a supercritical fluid is significantly different from one solute to another. Thus, by choosing the appropriate conditions, it may be possible to selectively extract a particular solute, or class of solutes. This would preclude the need for the sample cleanup step described above. The application of supercritical fluids in the selective extraction of aromatics/alkanes, and polycyclic aromatic hydrocarbons/polychlorinated biphenyls has been documented in the literature [1,2].

Carbon dioxide is the primary solvent used in the supercritical fluid extraction of organics because its critical point is easily attained in the laboratory, and because it is not toxic. There has been considerable interest recently in the use of two component supercritical solvents. Again, the primary solvent used is carbon dioxide, but the second solvent (the co-solvent) is usually an organic liquid. The role of the co-solvent is to increase the solubility or selectivity of a particular solute or class of solutes. Thus, in the extraction of organics from soils [1], the proportion of aromatics in the extract increased as the co-solvent was changed from a less polar to a more polar one. Methanol is a popular choice for co-solvent, both in supercritical fluid extraction and in supercritical fluid chromatography.

The supercritical fluid extraction apparatus was built in the laboratory. It consists of a pump, a pressure gauge, an extraction cell with an internal volume of approximately 0.3 mL, and a fused silica capillary restrictor (id 20 μ m). Carbon dioxide is used as the solvent. The extract is carried from the extraction cell through the capillary restrictor into a tube containing a small amount of liquid organic solvent (e.g. dichloromethane), where the carbon dioxide vaporizes, leaving the extracted compounds in the liquid solvent. The extract is then analyzed by gas chromatography.

The results of our investigations demonstrate that the supercritical fluid extraction technique using carbon dioxide yields rapid and quantitative recovery of polycyclic aromatic hydrocarbons from various environmental solids. The work is progressing to establish conditions to selectively extract various classes of organic compounds. The use of other pure solvents, as well as binary solvents will be studied. Other variables to be investigated are temperature, pressure, method of contacting the solid with the fluid, time of contact, and solvent flow rate.

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